Intrinsic Limit of Dielectric Loss in Several Ba(B1/3B2/3)O3 Ceramics Revealed by the Whispering-Gallery Mode Technique

Article *in* Applied Physics Letters · November 2005

DOI: 10.1063/1.2135379

CITATIONS
20

READS
66

3 authors:

Taras Kolodiazhnyi
National Institute for Materials Science
133 PUBLICATIONS **2,602** CITATIONS
SEE PROFILE

Giuseppe Annino
Istituto per i Processi Chimico Fisici, CNR
63 PUBLICATIONS **638** CITATIONS
SEE PROFILE

Takeshi Shimada
Hitachi Metals
44 PUBLICATIONS **679** CITATIONS
SEE PROFILE

Intrinsic limit of dielectric loss in several $Ba(B'_{1/3}B''_{2/3})O_3$ ceramics revealed by the whispering-gallery mode technique

T. Kolodiazhnyi[a)]
National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

G. Annino
Istituto per i Processi Chimico-Fisici, CNR, Pisa 56124, Italy

T. Shimada
R & D Center, Neomax Co., Ltd., Osaka 618-0013, Japan

(Received 16 August 2005; accepted 27 September 2005; published online 17 November 2005)

Whispering-gallery mode spectroscopy is employed to study the dielectric permittivity and losses of $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Nb_{2/3})O_3$, and $Ba(Co_{1/3}Nb_{2/3})O_3$ ceramics in the frequency range of 40–90 GHz and temperature interval of 5–295 K. Below 50 GHz, the room-temperature extrinsic dielectric losses in $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Nb_{2/3})O_3$ manifest themselves as a sublinear loss factor $\tan\delta(\omega)$ dependence until the intrinsic losses start to dominate the spectra around 50–70 GHz. Based on these data we obtain the room-temperature intrinsic limit of dielectric loss of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ($Q\times f=430\pm20$ THz) and of $Ba(Mg_{1/3}Nb_{2/3})O_3$ ($Q\times f=230\pm20$ THz). In the case of $Ba(Co_{1/3}Nb_{2/3})O_3$, the extrinsic losses were predominant throughout the studied frequency range. The possible sources of this loss are discussed. © *2005 American Institute of Physics*.
[DOI: 10.1063/1.2135379]

Over the last 10 years, we have witnessed wireless communications become a multibillion dollar industry. Despite competition with surface/bulk acoustic waveguides and high-T_c superconductor-based devices, dielectric resonators remain the primary components of base station filters for third- and ultimately fourth-generation cellular phones.[1] A preliminary knowledge of the intrinsic limit of the loss factor $\tan\delta$ is crucial for the fast screening of novel dielectrics as well as for the ultimate perfection of the already existing dielectric resonator (DR) materials.

As revealed by far infrared spectroscopy[2] and later confirmed by microwave studies at cryogenic temperatures,[3] the major contribution to the microwave dielectric loss of commercial DRs is of extrinsic origin (e.g., lattice disorder, point defects, dislocations, grain boundaries, secondary phases). For some time, the lower limit of the dielectric loss at microwave frequencies has been extrapolated from the far infrared data.[2] Although this approach gives a good estimate of the intrinsic dielectric loss in well-processed ceramics, the accuracy of this method is not so high since it involves extrapolation over two to three decades of frequency. Recently, a more accurate determination of the dielectric loss has been utilized using terahertz transmission spectroscopy.[4] According to that study, a well-processed $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramic with $Q\times f=330$ THz at 10 GHz shows predominantly intrinsic dielectric loss ($Q\times f\approx450$ THz) at as low as 300 GHz. Hence, it appears that the most interesting frequency band where the primary source of dielectric loss changes from extrinsic to intrinsic should lie in the 10–300 GHz range.

In this letter we report on the dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Nb_{2/3})O_3$ and $Ba(Co_{1/3}Nb_{2/3})O_3$ (hereafter abbreviated as BMT, BMN, and BCN, respectively) in the 40–90 GHz range using the whispering-gallery mode (WGM) technique based on unshielded resonators. For the first time we are able to demonstrate the transition from a sublinear to a linear $\tan\delta(\omega)$ dependence, indicating a change from the extrinsic to the fundamental type of dielectric loss in these technically important ceramics.

Samples of BMT, BMN, and BCN were prepared by a solid-state reaction from metal oxides and carbonates of 99.99 % purity. The mixtures were calcined at 950–1200 °C in air for 20 h. The calcined powders were milled for 24 h, pressed into pellets and sintered at 1290–1600 °C in air. The sample pellets were used as DRs for their dielectric characterization. In particular, the dielectric properties were measured at 10 GHz ($TE_{01\delta}$ mode technique) using an HP 8510 vector network analyzer and at 20–100 GHz (whispering-gallery mode technique) using an AB Millimetre vector network analyzer.

The WGM analysis was developed assuming no preliminary knowledge of the complex dielectric permittivity.[5] In this case, an *ab initio* approach was used in order to identify each resonance mode without mapping the field distribution and to clarify whether the dielectric properties of the material are isotropic. The latter point was addressed by measuring the two families of the resonance modes in cylindrical whispering gallery dielectric resonators, namely WGE (quasi-TE) and WGH (quasi-TM); the polarizations of these two families are in general almost orthogonal to each other, permitting the characterization of both components of the real and imaginary parts of the permittivity of a uniaxial material (four unknowns). The former point was solved by detecting the resonance modes in the lower limit of the working frequency band of the resonator, which is characterized by the presence of only the fundamental modes $WGM_{n,0,0}$. In this limit, the modal index of each mode can be determined with a self-consistent procedure based on the resonance frequency of several consecutive resonances. Once the fundamental modes of both families were identified, they were followed towards higher frequencies, where the spectrum becomes

a)Electronic mail: kolodiazhnyi.taras@nims.go.jp

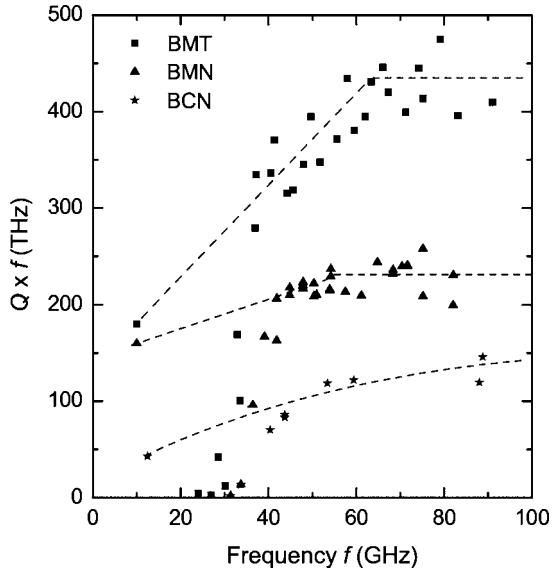

FIG. 1. Frequency dependence of $Q\times f$ for BMT, BMN, and BCN at 295 K. The dashed lines connect the low-frequency $TE_{01\delta}$ data and the high-frequency WGM data, and ignore the low-frequency WGM data determined by the radiation loss.

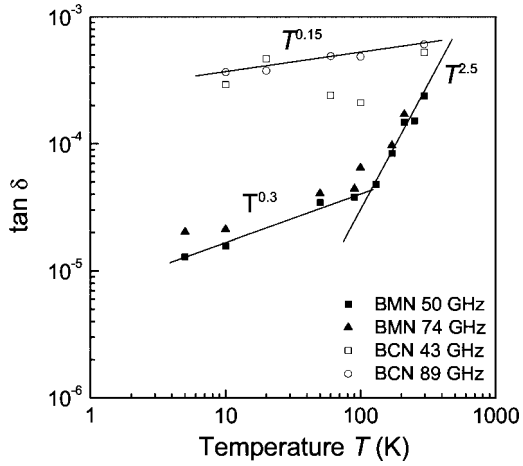

FIG. 2. Temperature dependence of tan δ of BMN and BCN at various frequencies.

more dense and the identification of the modes quite difficult. This approach allows the determination of the fraction of electric energy stored in the sample, and then the calculation of the loss factor from the unloaded quality factor Q. This latter quantity is limited, in unshielded resonators, by dielectric and radiation losses alone. The unloaded Q factor was obtained by a proper rescaling of the measured loaded Q_L factor, taking into account the degree of coupling of the radiation to the resonator. All fits of the Q factor were done in a complex plane, i.e., taking into account both amplitude and phase of the transmitted wave. The details and the complete results of this analysis will be presented elsewhere.

Figure 1 shows $TE_{01\delta}$ and WGM data of the BMT, BMN, and BCN ceramics at 295 K. As evidenced from the low $Q\times f$ value of 180 THz at 10 GHz, the BMT ceramic was not well processed. The BMT WGM data collected in the 22–90 GHz range shows several interesting features. In the 22–38 GHz range, the $Q\times f$ is limited by the radiation losses that occur in $WGM_{n,m,l}$ with a low azimuthal index n.[6] These losses exponentially decrease with an increase in n as the circulating electromagnetic wave approaches the total internal reflection limit at around 40 GHz. Above 40 GHz, the $Q\times f$ is determined by the internal dielectric losses of the BMT. The most remarkable feature in the 40–90 GHz range is a change in the slope of the $Q\times f$ dependence, as indicated by the dashed line in Fig. 1. According to the classical damped harmonic oscillator model, in perfect crystals the tan δ increases linearly with frequency below the fundamental phonon eigenfrequencies.[2] This translates into a frequency-independent $Q\times f$. According to this model, a steady increase of the $Q\times f$ of the BMT in the 40–65 GHz interval is assigned to the extrinsic contribution to the dielectric loss. Above 65 GHz the $Q\times f$ reaches a plateau at 430 ± 20 THz. We attribute this plateau to the *intrinsic limit* of the dielectric loss of BMT. This value is in reasonable agreement with the $Q\times f\approx 450$ THz obtained by the terahertz transmission spectroscopy at 300 GHz.[4] Extrapolation of the far-infrared data of Sagala[7] down to the 100–300 GHz also agrees fairly well with both the submillimeter wave results of Petzelt[4] and our WGM millimeter wave data.

The BMN sample measured at 10 GHz using the $TE_{01\delta}$ mode showed $Q\times f=160$ THz and dielectric permittivity of 31.5. The sample contained a small amount of $MgNb_2O_6$ and a secondary phase probably located along the $Ba_{2.5}Nb_5O_{15}-Ba_3Nb_5O_{15}$ tie line. Another attempt to obtain single phase BMN resulted in $Q\times f=178$ THz, although traces of the secondary phase could not be eliminated completely. Similar to the BMT behavior, the $Q\times f$ of the BMN WGM resonator increases sharply in the frequency range dominated by the radiation loss (20–40 GHz), followed by a more gradual increase in the 40–60 GHz interval (Fig. 1). Above 70 GHz, the $Q\times f$ of BMN tends to saturate at 230 ± 20 THz. It is remarkable that such a high $Q\times f$ can be achieved in BMN, which so far has been considered a high-loss material.[8] As of today, the $Q\times f=178$ THz is the highest reported value for tantalum-free $Ba(B'_{1/3}B''_{2/3})O_3$ perovskites in the X band. It is also of note that such a high $Q\times f$ was achieved without adding any "sintering aids" or "1:2 domain boundary stabilizers,"[9] which, in our opinion, are detrimental for the Q factor.

The $Q\times f$ data of the BCN sample are also shown in Fig. 1. At 12 GHz, the BCN sample has $Q\times f=42$ THz and a dielectric permittivity of 31.2. Unlike the BMT and BMN samples, the BCN resonator shows a continuous increase in $Q\times f$ within the 10–100 GHz frequency interval, without a noticeable saturation of the $Q\times f$. Hence, we conclude that the dielectric loss in this BCN sample is dominated by the extrinsic sources throughout the studied frequency range.

Measurement of the temperature dependence of tan δ is another way to distinguish between extrinsic and intrinsic dielectric loss. According to the theory of the dielectric loss, a power-law dependence of tan δ on temperature is expected to hold in the case of intrinsic loss (i.e., tan $\delta\propto T^m$ where m depends on the crystal symmetry of the compound).[10] In most cases of intrinsic dielectric loss in single crystals and ceramics, $m>2$ is observed. The temperature dependence of tan δ of BMT has been measured by Alford *et al.*[11] at 8.34 GHz in the temperature interval of 10–300 K, which revealed extrinsic-type behavior with $m\approx 0.6$. We measured the temperature dependence of tan δ in the BMN and BCN ceramics in the millimeter wave range (Fig. 2). The BMN shows a typical intrinsic-type behavior with a steep decrease

in tan δ as the temperature is lowered from 300 to 100 K. This behavior of dielectric loss with tan $\delta \propto T^{2.5}$ is attributed to a decrease in the phonon density of states at low temperatures and extinction of the two-phonon-difference absorption process.[12] Below 100 K, the intrinsic dielectric losses of BMN become smaller than the extrinsic losses manifested by a weak temperature dependence with $m=0.3$.

In contrast to BMN, the temperature dependence of tan δ of the BCN sample indicates an extrinsic character of the dielectric loss in the full 10–300 K range, in accordance with the frequency dependence of the $Q \times f$ shown in Fig. 2. Since we have not detected any second phases in the BCN sample, we suggest that the possible sources of the extrinsic dielectric loss in BCN are related to the various chemical states of the Co^{2+} ion. It is known that Co^{2+} may exist in both low spin ($t_{2g}^6 e_g^1$) and high spin ($t_{2g}^5 e_g^2$) configurations in an octahedral crystal field, which may result in a complex Jahn-Teller distortion pattern of the oxygen ligands, especially near the domain walls, grain boundaries, or other structural defects, and provide a new channel for the electromagnetic absorption in the millimeter wave range. Another possibility of extrinsic loss in BCN is due to absorption by the Co_{Nb} antisite defect. This defect can easily be stabilized by the oxygen vacancy V_O to form an extended $Co_{Nb}-V_O$ defect complex. There are 51 possible types of intrinsic lattice defect and binary defect complex in $Ba(B'_{1/3}B''_{2/3})O_3$ perovskites.[13] Unfortunately, in contrast to the simple ABO_3 perovskites, the formation energy of lattice defects in $Ba(B'_{1/3}B''_{2/3})O_3$ has been studied neither theoretically nor experimentally.

In conclusion, we determined the intrinsic limit of the dielectric loss in BMT and BMN ceramics taking advantage of the unshielded WGM resonators millimeter wave spectroscopy. We have also addressed the possible sources of the extrinsic dielectric loss in the BCN ceramics.

Part of this study was performed through Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.

[1] H. Hughes, D. M. Iddles, and I. M. Reaney, Appl. Phys. Lett. **79**, 2952 (2001).
[2] J. Petzelt and N. Setter, Ferroelectrics **150**, 89 (1993).
[3] N. McN. Alford, J. Breeze, X. Wang, S. J. Penn, S. J. Webb, N. Ljepojevic, and X. Aupi, J. Eur. Ceram. Soc. **21**, 2605 (2001).
[4] J. Petzelt and S. Kamba, Mater. Chem. Phys. **79**, 175 (2003).
[5] G. Annino, D. Bertolini, M. Cassettari, M. Fittipaldi, I. Longo, and M. Martinelli, J. Chem. Phys. **112**, 2308 (2000).
[6] G. Annino, M. Cassettari, and M. Martinelli, Int. J. Infrared Millim. Waves **23**, 597 (2002).
[7] D. A. Sagala and S. Koyasu, J. Am. Ceram. Soc. **76**, 2433 (1993).
[8] S. Nomura, Ferroelectrics **49**, 61 (1983).
[9] M. A. Akbas and P. K. Davies, J. Am. Ceram. Soc. **81**, 670 (1998).
[10] V. B. Braginsky, V. S. Ilchenko, and Kh. S. Bagdassarov, Phys. Lett. A **120**, 300 (1987).
[11] N. McN. Alford, S. J. Penn, A. Templeton, and X. Wang, J. Supercond. **10**, 467 (1997).
[12] V. L. Gurevich and A. K. Tagantsev, Adv. Phys. **40**, 719 (1991).
[13] T. Kolodiazhnyi, G. Annino, A. Younker, P. Malysz, P. Mascher, and H. Haneda, J. Eur. Ceram. Soc. (to be published).